[redacted]

(NASA CR-50952)

OTS: $4.60 ph, $1.49 mf

Interim Technical Report No. 1, October 1962 to June 1963

SPACE ENVIRONMENT EFFECTS ON POLYMERIC MATERIALS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950324
UNDER NAS7-100

(NASA Contract NAS7-100; JPL Contract 950324; SRI Proj: PLU-4257)

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

*SRI

STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

D. L. Chamberlain et al June 8, 1963
143p (Orf)

Interim Technical Report No. 1 | *October 1962 to June 1963*

SPACE ENVIRONMENT EFFECTS ON POLYMERIC MATERIALS

JPL CONTRACT NO. 950324 UNDER NAS7-100

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL Cognizant Engineer: Robert Harrington

SRI Project No. PLU-4257

Approved:

R. F. Muraca

R. F. MURACA, ASSISTANT GENERAL MANAGER
PHYSICAL SCIENCES RESEARCH

Copy No. 87

ACKNOWLEDGEMENTS

Contributions to this report were made by:

D. L. Chamberlain

L. D. Christensen

N. Fishman

M. A. Golub

J. Heller

D. J. Lyman

R. F. Muraca

J. S. Whittick

Program Co-ordinator: J. S. Whittick

CONTENTS

LIST OF ILLUSTRATIONS

TABLES

I INTRODUCTION AND SUMMARY

This Interim Technical Report No. 1 summarizes the work done under JPL Contract No. 950324, SRI Project No. PLU-4257, during the period October 1 to November 6, 1962 and January 17 to May 31, 1963.

The objective of this program of work is to provide a definitive study of the effect of high vacuum (pressures greater than 10^{-8} mm of Hg) and temperatures in the range of 400 to 550°K on polymeric materials which are suitable for use in spacecrafts. The program is designed: (1) to determine changes in pertinent physical properties of selected polymers, (2) to determine, if possible, modes of polymer degradation in space environment, and (3) to ascertain the extent to which warm polymers in a vacuum release substances which are condensable at temperatures in the vicinity of 25°C.

The materials being studied are laboratory-prepared (or purified) polymers and commercial polymers such as Teflons, Vitons, Mylars, polyamides, and silicone rubbers.

The procedure and preliminary results of the study of polymer degradation by means of mass spectrometry are discussed in Section II of this report. Analysis of material evolved by a sample of laboratory-prepared Nylon-6 indicate that the materials volatilized during the initial heating and evacuation are ϵ-caprolactam and water.

The design of the apparatus which is being used for the volatile condensable material (V.C.M.) study is described in Section III; drawings and photographs are included. A preliminary run on a silicone rubber has been completed; oily material was collected.

Section IV includes an outline of the synthetic routes for preparation of Nylon-6 and the polyurethanes which will be used for the determination of the mechanisms of chemical degradation of polymers in a simulated space environment. The pyrolysis chamber and vacuum assembly which will

be used to study the degradation of Nylons has been completed. The thermal degradation of polyurethanes in vacuum has been followed by infrared spectroscopy, and a tentative mechanism for the degradation of one of the polyurethanes is given.

The test program for determining changes in mechanical properties of polymers subjected to a vacuum-thermal environment is outlined in Section V, and a description is given of apparatus constructed for the various tests. Stress-relaxation and creep tests are underway in a vacuum chamber; the stress-relaxation and creep measurements are made in situ. The tensile properties at constant strain rate (Instron) of the candidate polymers will be determined before and after storage in a vacuum-thermal environment. Comparative tests will be performed in inert gases and in air at one atmosphere and for periods as long as three months.

II MASS SPECTROMETER STUDY OF POLYMER DEGRADATION

Extensive studies have been conducted over the past twenty years on the pyrolytic degradation of polymers; the purpose of these studies has been to identify the products of decomposition and to detect structural changes. For the most part, these studies have involved rather rapid pyrolyses of polymeric materials at temperatures greater than 250°C in high vacuum or in air or oxygen atmospheres, with or without ultraviolet radiation. The volatilization of polymers in high vacuum and at lower temperatures (25-125°C), such as the environment of outer space, has not been given much attention except for occasional references to the possible release of occluded gases, residual monomer, excess moisture, etc.

The kinds of compounds released or formed by a polymeric material in a simulated space environment and the influence of this environment on the mode of chemical degradation are important considerations in the selection of polymers for spacecraft use. Since the commercial polymers which may be used in the spacecrafts as gaskets, sealants, potting compounds, etc. usually are not pre-treated to remove volatile material, it is the the purpose of this part of the program of study to determine the nature of the volatile material which is released from selected commercial polymeric substances in vacuum at temperatures up to 125°C; in addition, volatile material released from laboratory-prepared "pure" polymers will be determined. It is anticipated that these comparative studies will indicate whether there is any difference in the degradation modes between commercial and "pure" polymers, or if improvement of commercial formulations is possible.

One of the most direct methods of identifying materials which are released from a polymeric substance in a simulated space environment is by the use of mass spectrometry. The mass spectrometer is ideally suited for this type of analysis for the following major reasons:

(1) Only a very small sample is necessary (of the order of 5 milligrams);

(2) Polymeric substances, such as might be used in a spacecraft, generally have very low vapor pressures, and the sensitivity of the mass spectrometer permits analysis of materials at low pressures;

(3) The vapors released by the polymer can be scanned periodically without altering conditions of vacuum or temperature, and all gases present will appear in a single scan;

(4) Loss of sample or contamination, such as may result when vaporized materials are collected and transfered, is eliminated by direct analysis of volatilized material as evolved.

Apparatus

The mass spectrometer used in this work is a Consolidated Electrodynamics Corporation Model 21-103C which has been modified to include an additional sampling system between the normal inlet system and the analyzer tube; this system permits facile interchange of various sampling devices, operation with or without the gold (molecular) leak, a line-of-sight path directly into the analyzing region, and a small working volume (about 80 cc compared with the 3-liter expansion system). The mercury diffusion pump system generally employed for exhausting the analyzer region has been replaced with a 40-liter per second VacIon pump, and the oil diffusion pump on the inlet side has been replaced with a 15-liter per second VacIon pump. The replacement of the mercury pump eliminates cold-traps and traces of mercury vapor in the analyzing tube; replacement of the oil diffusion pump in the inlet side eliminates hydrocarbon contamination throughout the entire system. The vacuum attainable in the ion pump is better than 1×10^{-8} mm of Hg, the pressure on the pump side of the analyzing area is of the order of 1×10^{-7} mm of Hg, and the pressure in the ionizing region and sampling region is about 1×10^{-6} mm of Hg.

Because the polymers selected for this program of work exhibit low vapor pressures and rates of evaporation, the molecular leak between the sampling system and the ionizing region has been removed so as to increase the over-all sensitivity of the ion-gun. Samples of materials (5-6 mg) are placed in a 6-mm glass tube which is joined by a Kovar tube to the

stainless steel inlet part of the modified analyzer-tube assembly. Heat is applied to the tube by a small furnace and the temperature is controlled by an autotransformer.

Discussion

It has been established that two types of polymers would be studied during this program: (1) selected commercial polymeric materials, and (2) laboratory-prepared "pure" materials. Since a polyamide, namely Nylon-6, has been selected by the polymer group for extensive study of the mechanisms of degradation (See Section IV), the preliminary trial of the proposed mass spectrometer technique for identification of volatile material was conducted on a sample of Nylon-6 prepared by the polymer group.

The Nylon-6 was prepared by polymerizing ϵ-caprolactam (recrystallized from cyclohexane) with water at 265°C; polymerization was carried out in a sealed ampoule in a nitrogen atmosphere. After a reaction time of 6 hours, the tube was opened, water was removed, and the polymer dried under a stream of nitrogen for 2 hours at 250°C.

About 20 milligrams of the synthesized Nylon-6 was placed in the 6-mm glass tube of the sampling system of the mass spectrometer. The tube furnace was then moved into place around the sample tube, and the system was evacuated. After one hour, the pressure in the working volume (80 cc) was allowed to come to equilibrium, and then the mass spectrum was recorded from m/e 2 to m/e 360. The spectrum was obtained again after 5 hours and after 23 hours of evacuation time. Additional mass spectra were obtained at temperatures of 48, 96, and 125°C; each temperature was maintained until the spectra were scarcely different from the normal spectrometer background. Characteristic peak heights of some of the runs are given in Table II-1.

The largest pressure reading of the entire run was observed, as is to be expected, during the first hour of evacuation at 25°C. The major component of the volatile material was water; secondary components were ϵ-caprolactam monomer and dimer.

Table II-1

SELECTED MASS SPECTRAL PEAKS OF LABORATORY-PREPARED NYLON-6 AND COMMERCIAL NYLON-6

m/e	Lab-Prepared Nylon-6							Com'l Nylon-6		ϵ-Caprolactam
	25°C			125°C				25°C		
	1 hr	5 hr	23 hr	24 hr	30 hr	70 hr	118 hr	1 hr	2 hr	
18	355.0	68.8	20.5	14.8	10.3	6.0	4.4	633.0	350.6	47.3
28	42.8	27.0	22.0	198.0	56.0	17.4	15.4	52.4	33.0	110.4
30	3.3	0.9	0.4	293.0	64.5	2.8	0.8	5.8	1.4	116.7
32	11.8	9.8	7.3	6.5	6.2	5.9	6.0	12.2	10.0	15.2
44	25.7	6.4	3.4	19.7	6.2	2.0	1.6	30.3	19.0	9.5
55	10.3	2.3	1.0	236.7	54.8	2.6	0.8	5.7	1.8	92.3
84	1.0	0.7	0.3	113.4	31.0	0.8	0.4	1.0	0.4	45.3
113	0.6	0.5	0.2	162.6	47.8	1.1	0.5	1.6	0.5	66.5

The exposure at 48°C was maintained for only a few hours because no differences in spectra were observed and the total ion intensity was quite diminished. Again, the major component was water, and the secondary component was ϵ-caprolactam monomer. At 96°C, water and ϵ-caprolactam monomer were released in about equal quantities, and at 125°C, the major component was ϵ-caprolactam.

As this report was in production, a run on a commercial sample of Nylon-6 was begun. Some of the data on the preliminary evacuation are given in Table II-1, and it can be seen that the commercial sample has much less free ϵ-caprolactam than the laboratory-prepared sample.

III VOLATILE CONDENSABLE MATERIALS

The loss of material by evaporation or sublimation is one of the most obvious effects of a vacuum-thermal environment on polymers. Consequently, the polymers which are considered suitable for use in spacecrafts are those which exhibit a minimum loss of weight when exposed to the simulated conditions of the vacuum and thermal environment of space. However, it has been found that many polymers which, at first sight, appear to be satisfactory for use in spacecrafts because of low loss of material, when warm may release substances which condense on cooler surfaces and interfere with spacecraft functions. Condensation of materials on absorptive or emittive coatings, mirrors or lenses, and on electrical contact points are examples of these interferences.

Space probes and satellites are generally designed to maintain internal temperatures of the order of 25°C, but temperatures as much as 125°C may occur in the vicinity of power-dissipating components. Thus, a suitable polymer for spacecraft application must retain its properties at a temperature of 125°C in a vacuum and must release negligible amounts of material which condense on surfaces at 25°C. This section describes the construction of an apparatus for the determination of volatile condensable material, V.C.M., i.e., the amount of condensable material derivable from a polymeric substance maintained at a temperature of 125°C in a vacuum.

V.C.M. Apparatus

During the first six months of this program, the V.C.M. apparatus has been designed and fabricated. At appropriate stages of fabrication, the apparatus was checked for mechanical construction features and electrical efficiency, and modifications of original design were made as necessary. The heaters have been designed to deliver temperatures to 275°C with a variance between heaters of no more than 5°C; each heater is provided with thermocouples for temperature measurements. The working drawings for the apparatus are given in Figures III-1, III-7, III-8, and III-9.

A schematic drawing of a single unit for determining V.C.M. is shown in Figure III-1. A heavy-walled copper cylinder is welded to a copper water-cooled base plate; by conduction, the temperature of the heavy-walled cylinder is kept reasonably constant in the vicinity of 25°C (water temperature). A Nichrome wire heater, wound around a ceramic tube, is located axially within the heavy-walled copper cylinder. Supported around the heater is a copper sleeve to which can be attached the polymeric or elastomeric sample under study. At the mid-point of the heavy-walled copper cylinder is situated a polished tapered plug held in place by a screw-clamp (not shown in Figure III-1). In operation, the temperature of the central heater is controlled by an adjustable auto-transformer and an auxiliary resistance; the power input to the heater is regulated so as to maintain the temperature of the copper sleeve at 125°C as indicated by a copper-Constantan thermocouple. The whole unit is mounted within a vacuum chamber capable of maintaining a pressure of at least 1×10^{-6} mm of Hg. Material volatilized from the sample impinges on the cold heavy-walled copper cylinder and, if it is condensable at 25°C, will remain on the cylinder wall. Since the polished tapered plug is a segment of the cylinder wall, material will condense upon it in a similar fashion; the plug may be weighed beforehand on a microbalance, and after the test it may be reweighed to determine the amount of condensed material. Alternatively, since the tapered plug's surface is highly polished, discolorations or deposits may be detected visually. The relation of the area of heated sample and the surface area of the heavy-walled cylinder upon which material can condense by straight-line impingement permits computation of the amount of V.C.M. which a given material liberates.

As indicated in Figure III-1, a liquid nitrogen-cooled surface is maintained just above the V.C.M. unit. A series of baffles (A, B, C) are interposed between the liquid nitrogen-cooled surface and the upper edges of the heavy-walled copper cylinder in order to prevent its being cooled by radiation to the liquid nitrogen-cooled surface. Similarly, shields A, B, and C mounted loosely on a pin supported by the heater element prevent undue radiation and resultant cooling of the copper

sleeve and heater. The disposition of the shields and baffles are such as to minimize thermal gradients within the V.C.M. unit; however, sufficient clearances have been provided so that noncondensable materials emitted by the sample eventually can migrate out of the V.C.M. unit. Thus, the liquid nitrogen-cooled surface acts as a cryopump.

Although only one V.C.M. unit is indicated in Figure III-1, in order to permit replication of samples, a cluster of six identical units was constructed. Figure III-2 shows the arrangement of the cluster of six V.C.M. units and also shows the units in various stages of assembly. As can be seen in this figure, the six units are protected from the ambient environment in the vacuum system by two sharp-edged shields welded to the periphery of the water-cooled base plate.

Figure III-3 shows the arrangement of the three baffles, and Figure III-4 shows the appearance of the completed V.C.M. apparatus. The cluster of six V.C.M. units is supported on a lever arm which holds it in place under the liquid nitrogen-cooled surface but permits it to be swung out of the vacuum chamber for changing of samples. The liquid nitrogen-cooled surface is the flat bottom of a glass vessel having the same diameter as the baffles.

Figure III-5 is a detailed view of the heater and sleeve assembly for a V.C.M. unit. The complete apparatus for V.C.M. determination is indicated in Figure III-6; as can be seen in this figure, the vacuum chamber is an aluminum box with an 18-inch diameter Lucite window and entry port. The vacuum system is a compact unit comprising a Welch Duo-Seal forepump (No. 1397B), a 6-inch oil diffusion pump (CEC Model MCF-700), and a manually-operated valve (CVC Type VT-SB-61). A 6-inch line connects the chamber to a low-loss trap directly connected to the outlet of the valve. Suitable by-passes and ball valves permit "roughing" the vacuum chamber and "holding" the diffusion pump during preliminary evacuation procedures. A Pirani gage and an ionization gage (VG-1A) are used for measuring the vacuum in the chamber. The vacuum chamber can easily be evacuated to at least 1×10^{-6} Torr and to 5×10^{-7} Torr with operating traps.

The V.C.M apparatus cluster was checked preliminarily in a vacuum of the order of 1 micron; a final check was made at 10^{-6} mm of Hg. In order to obtain a check of the operation of the ending apparatus, strips of a G.E. silicone rubber (red) were fastened to the heaters in the cluster and, after preliminary evacuations to 5 x 10^{-6} mm of Hg (4-5 hours), the heaters were turned on ($125^{\circ}C$) and liquid nitrogen cooling was initiated. After 30 hours, the run was discontinued. Figure III-10 shows the appearance of one of the polished tapered plugs; oil droplets and some discoloration of the polished surface were clearly evident.

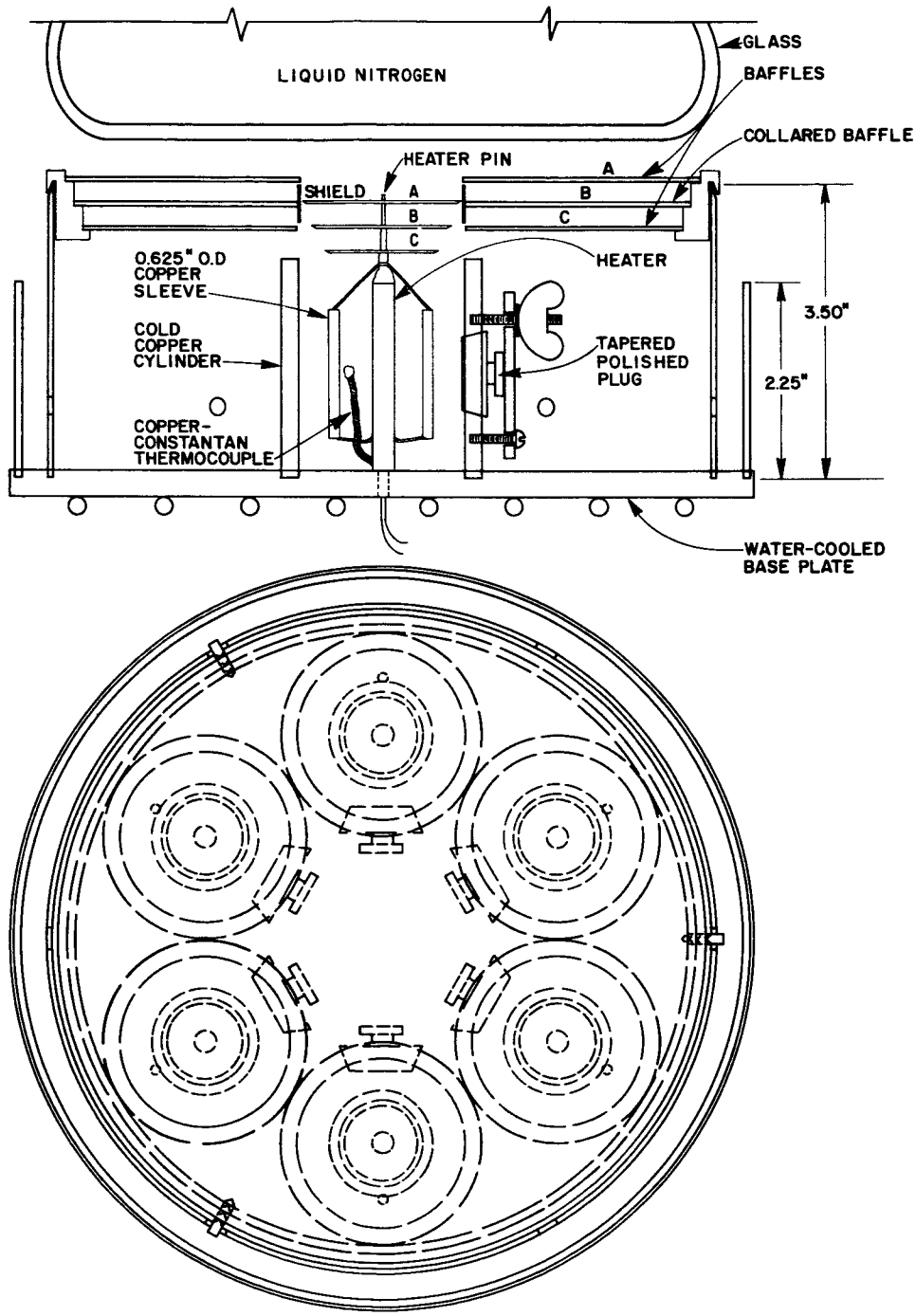


FIG. III-1 SCHEMATIC DIAGRAM OF A SINGLE VCM UNIT AND ARRANGEMENT OF A CLUSTER OF SIX UNITS

FIG. III-2 INTERNAL VIEW OF VCM APPARATUS SHOWING ARRANGEMENT OF HEATER-COLLECTOR ASSEMBLIES AND SHIELDS

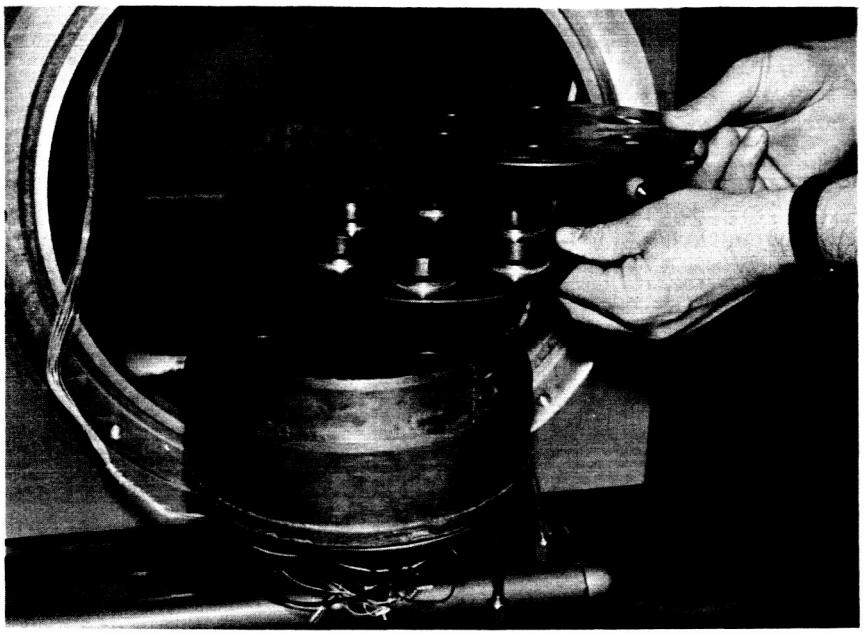


FIG. III-3 THE ASSEMBLY OF THE VCM APPARATUS SHOWING ARRANGEMENT OF BAFFLES

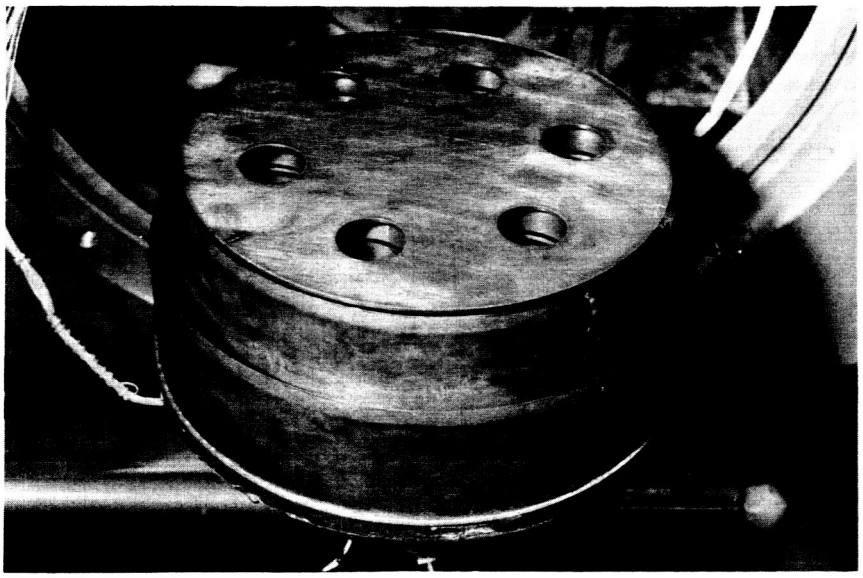
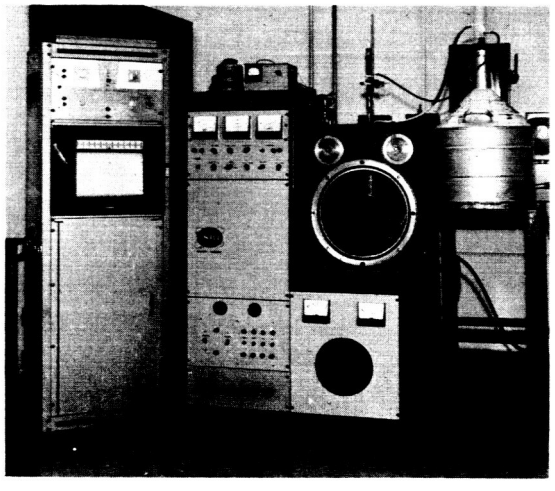


FIG. III-4 COMPLETED ASSEMBLY OF THE VCM PLATES

FIG. III-5 HEATER AND SHIELD ASSEMBLY FOR VCM

FIG. III-6 COMPLETE APPARATUS FOR VCM DETERMINATION



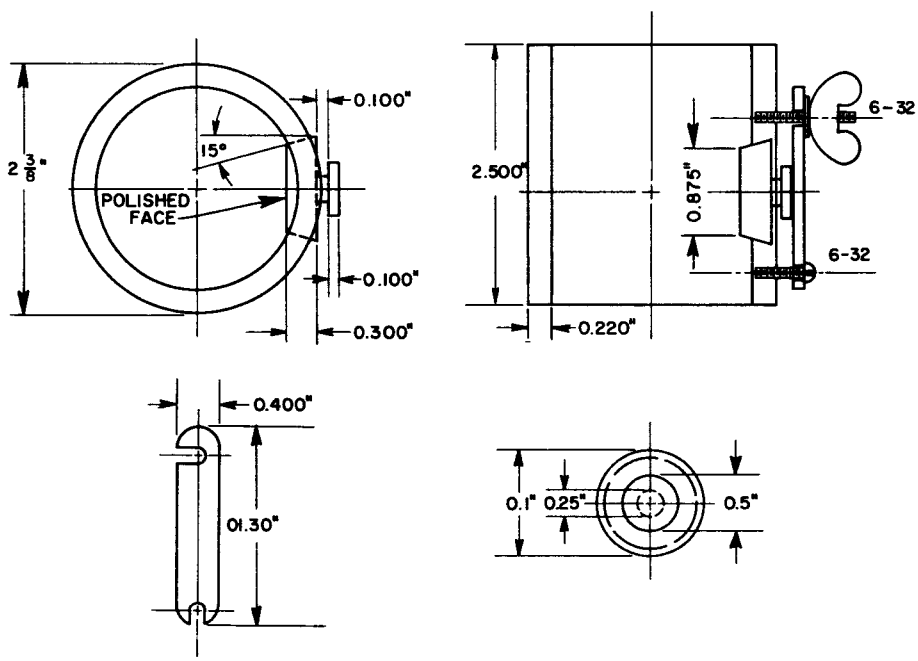


FIG. III-7 SCHEMATIC OF COLD COPPER CYLINDER

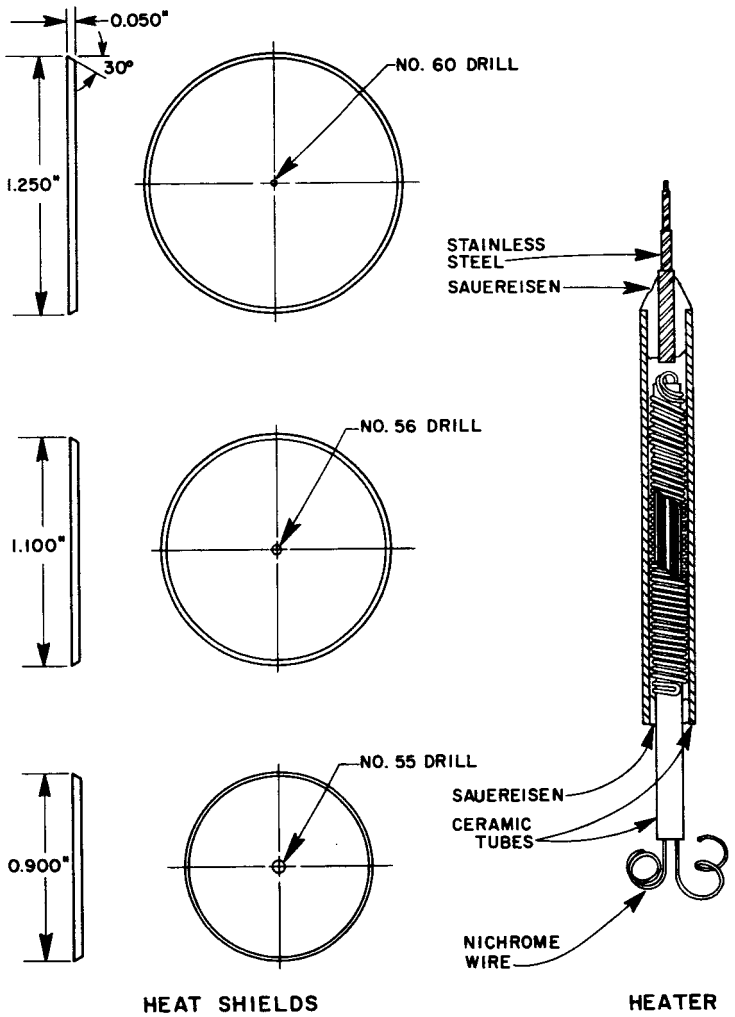
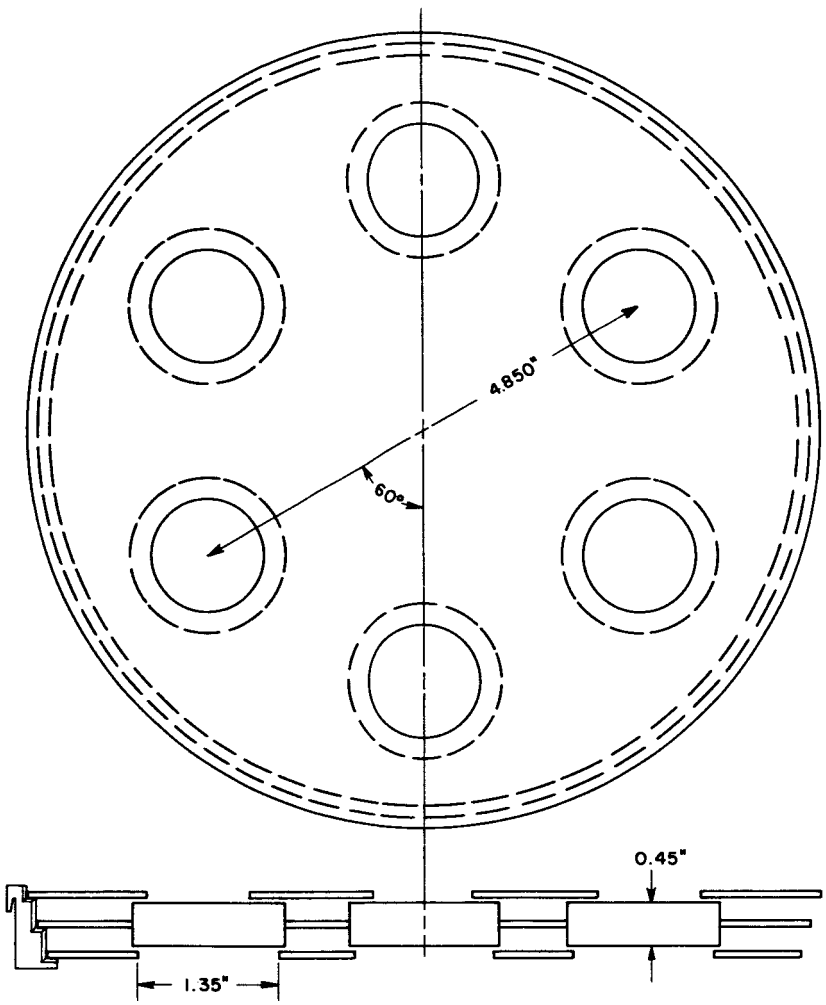
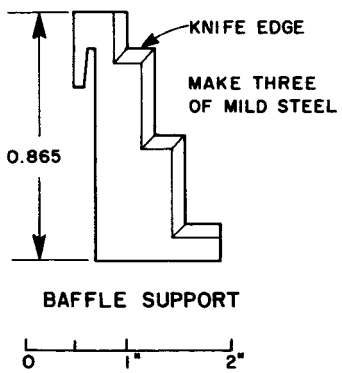


FIG. III-8 HEATER AND HEAT SHIELDS



BAFFLE ASSEMBLY



BAFFLE SUPPORT

FIG. III-9 BAFFLE SUPPORT AND BAFFLE ASSEMBLY

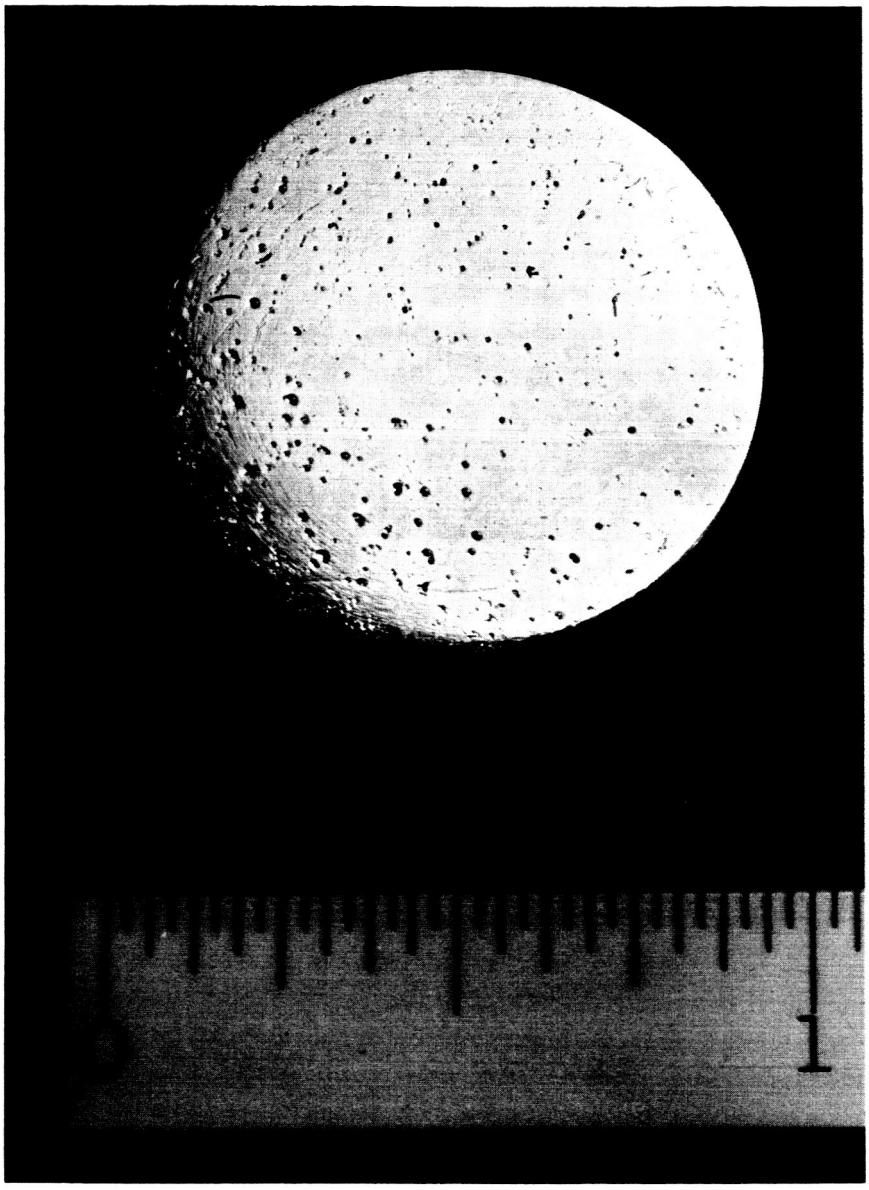


FIG. III-10 CONDENSED MATERIAL ON A POLISHED TAPERED PLUG OBTAINED ON A PRELIMINARY RUN WITH A SILICONE RUBBER. TINY DROPLETS OF OIL ARE VISIBLE; SOME DISCOLORATION OF COPPER PLUG IS DISCERNIBLE ON THE ORIGINAL; WEIGHT OF COLLECTED MATERIAL, 0.4 mg

IV POLYMER SYNTHESES AND DEGRADATION STUDIES

The determination of the mechanisms of chemical degradation of polymeric materials subjected to conditions of high vacuum and elevated temperature is one of the objectives of this program of work. Two types of polymers have been selected for extensive study: (1) polyamide and (2) polyurethane.

The polyamide degradation study involves the synthesis of Nylon-6 by different routes, and the synthesis of deuterated Nylon-6. Since the mechanisms of the chemical degradation below pyrolysis temperatures has been a subject of intensive study by many workers, initial studies are concerned with an attempt to correlate the data resulting from differential thermal analysis, thermogravimetric analysis, and gas chromatography with published data; a study of the deuterated Nylon-6, including infrared and mass spectrometer determinations, will provide insight into skeletal degradation under vacuum-thermal conditions.

The polyurethane degradation study, involving the synthesis of two selected polyurethanes, is concerned primarily with following vacuum-thermal degradation by means of infrared spectroscopy, and additional identification of degradation products by mass spectroscopy.

Apparatus

The vacuum system which will be used for studies of polymer degradation has been completed; the system employs a CVC MCF-300 diffusion pump and a Welch Duo-Seal Model 1402 forepump. Preliminary measurements have indicated a pressure of $< 10^{-7}$ mm of Hg, after a pump-down and bake-out period of 5 hours. A Toepler pump and gas burette has been installed in the system in order to collect and measure noncondensable gases; the measurement and analysis of the condensable material and noncondensable gases will permit the calculation of a mass balance for the products of degradation.

Synthesis and Degradation of Nylons

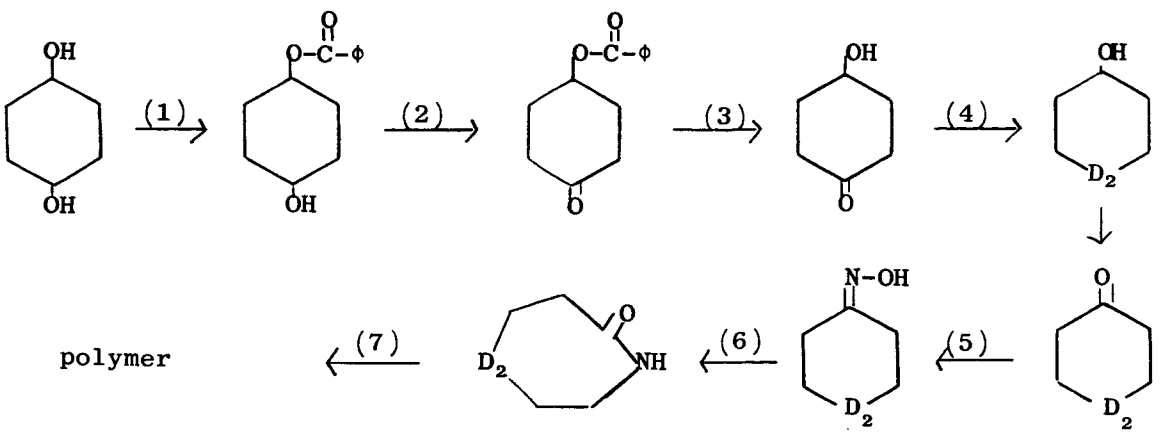
2-Oxohexamethylenimine. This intermediate was obtained from the Matheson Chemical Co., recrystallized several times from carefully purified cyclohexane, dried 24 hours at 1 mm of Hg in a vacuum oven, and stored in a dessicator.

Nylon-6. 2-Oxohexamethylenimine was converted to Nylon-6 by treatment for 6 hours at 250°C[1] with a catalytic amount of water in a sealed glass ampoule containing a nitrogen atmosphere. Following this treatment, the ampoule was opened, the water was removed, and the residue was flushed with dry nitrogen for 4 hours at 255°C. Then, the ampoule was broken to free the milky-white plug of polymer. The inherent viscosity of a solution of this Nylon in m-cresol was 0.96, which corresponds to a number-average molecular weight of 10,000-12,000.

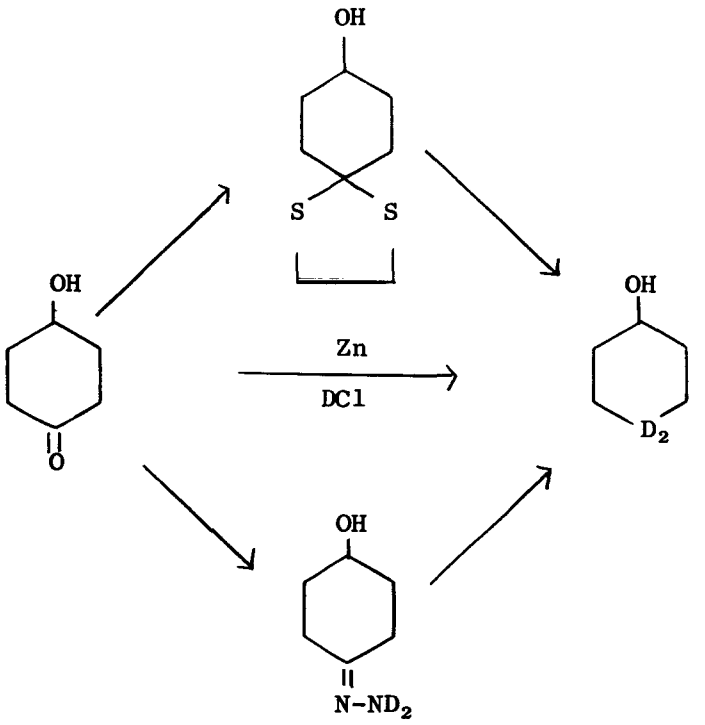
2-Oxohexamethylenimine-Nd. Repeated equilibration of a cyclohexane solution of 2-oxohexamethylenimine with D_2O in the presence of D_2SO_4 resulted in 85% replacement of the N-H groups with N-D groups, as shown by the NMR spectrum.

Nylon-6-Nd. 2-Oxohexamethylenimine-Nd was converted to the N-deuterated Nylon by the method described above for Nylon-6. Viscosity measurement and NMR determination of the deuterium content are in progress.

Nylon-6-4d_2, $+NH-CH_2CH_2-CD_2-CH_2CH_2-\overset{O}{\overset{\|}{C}}+_n$. This compound is now being synthesized by the following route:



Present efforts of this phase are now on the deuteration step for which three different methods are available; these are depicted below:



Evaluation of literature data indicate that a Clemenson reduction (Zn, DCl) is the simplest route provided that no difficulties arising from the hydroxyl group are encountered. The route involving Raney nickel desulfurization has recently been reported to yield a mixture of dideutero, monodeutero and perdeutero products. A reduction with deuterohydrazine, involving the reflux of a ketone with excess deutero-hydrazine, has also recently been reported; this could represent a simple, but expensive method.

Nylon-6-6d_2; $\text{-[NH-CD}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{-C(=O)-]}_n$. This compound is now being synthesized by the following route:

$$NC(CH_2)_4CN \xrightarrow{(1)} NC\text{-}(CH_2)_4\text{-}C(=O)\text{-}NH_2 \xrightarrow{(2)} D_2N\text{-}CD_2(CH_2)_4\text{-}C(=O)\text{-}NH_2$$

$$\text{polymer} \xleftarrow{(5)} H_2N\text{-}CD_2(CH_2)_4\text{-}C(=O)\text{-}Cl \xleftarrow{(4)} H_2N\text{-}CD_2(CH_2)_4\text{-}C(=O)\text{-}OH \quad \downarrow(3)$$

Present efforts of this phase are on the hydrogenation step. It was found that rhodium on alumina is an excellent hydrogenation catalyst; however, a number of problems still need to be worked out. It is known that the hydrogenation of nitriles leads to a mixture of primary and secondary amines. This arises from the fact that the hydrogenation of a nitrile proceeds via the intermediate reduction to an imine which then adds another mole of hydrogen. Unfortunately, however, the imine can also add a mole of amine, thus giving rise to a secondary amine:

$$R\text{-}C{\equiv}NH + R\text{-}NH{=}NH \rightarrow R\text{-}CH_2\text{-}NH_2$$

$$R\text{-}CH{=}NH + R\text{-}NH_2 \rightarrow R\text{-}CH_2\text{-}NH\text{-}R + NH_3$$

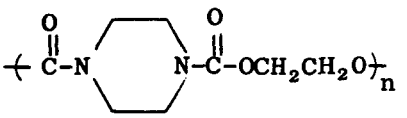
In the present case, the separation of primary and secondary amine products is difficult due to the extreme hygroscopic nature of the desired primary amine.

The present approach is to carry out the hydrogenation at a relatively high pressure of 30-50 atm so as to reduce the lifetime of the intermediate imine, and to hydrolyze the crude reaction product to the acid which, unlike the amine, is not hygroscopic.

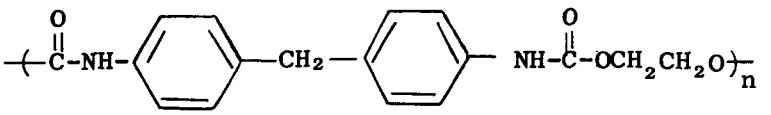
No degradation studies have yet been undertaken on Nylon samples.

Synthesis and Degradation of Polyurethanes

Initial studies are concerned with the degradation of the following polyurethanes:

I  Pip-2U

and

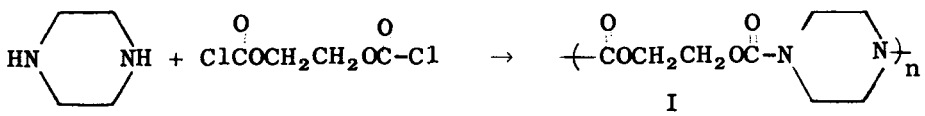
II  . DDM-2U

Pip-2U(polyurethane I) was chosen for initial study because of its structural relationship to polyethylene terephthalate.[2-5] It was hoped that the knowledge available on polyethylene terephthalate degradation

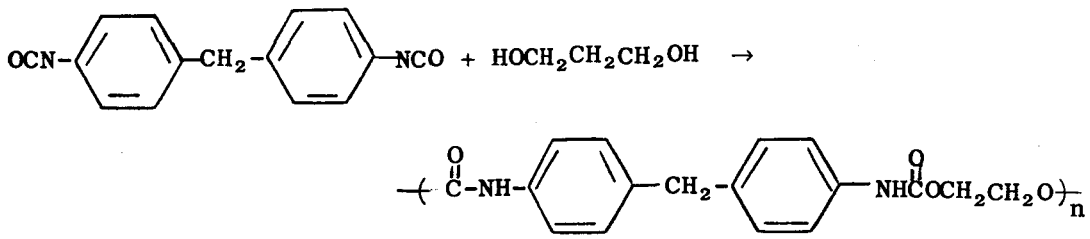
would prove valuable in determining the mechanism of polyurethane degradation.

DDM-2U (polyurethane II) was chosen for the second polymer to be degraded since it represents a molecular structure equivalent to that found in commercial polyurethanes.

Synthesis: The polyurethanes were prepared by interfacial polycondensation techniques[6-8] and solution polymerization techniques.[9] For example,



I

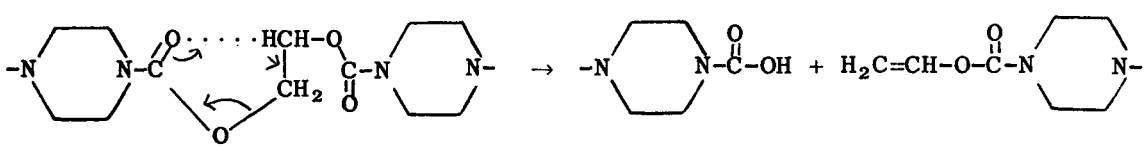


II

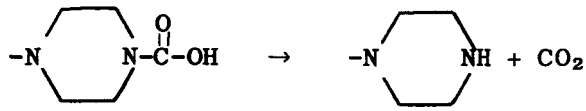
Degradation: Films of the polymers were cast on salt plates, and the thermal-vacuum degradation was followed by observing the changes in infrared spectra. For DDM-2U, no degradation occurred up to 156°C but was definitely discernible at 179°C. For Pip-2U, no degradation occurred up to 222°C but was evident at 242°C. Cell pressure during these studies was of the order of 10^{-4} to 10^{-5} mm of Hg.

Preliminary qualitative data (infrared and mass spectroscopy) on the product obtained from the degradation of Pip-2U at 255°C/0.01 mm indicate a mechanism similar to that shown by polyethylene terephthalate:

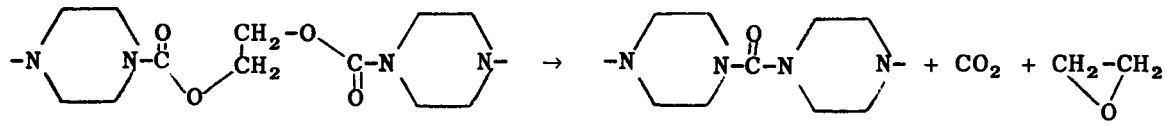
(1) Major alkyl-oxygen scission,



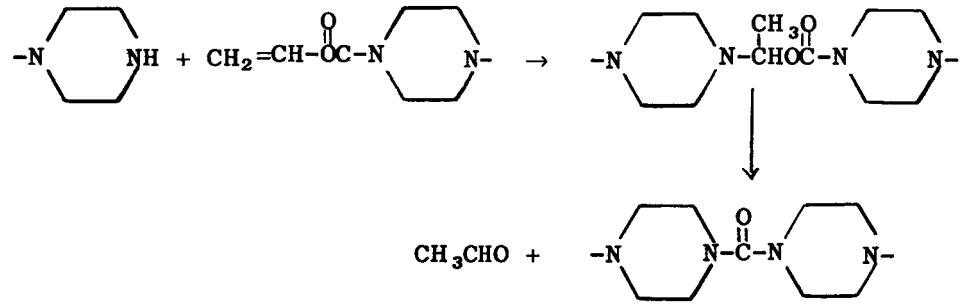
(2) Degradation of carbamic acid derivatives,



(3) Minor disproportionation,



(4) Amine-vinyl ester reaction,



Additional quantitative data on the by-products are being obtained. The polymer residue is not cross-linked and appears to reach a limiting size with no further degradation occurring. This material is being studied in more detail to confirm its structure.

References

1. Sorenson, W. R., and Campbell, Tod. W., Preparative Methods of Polymer Chemistry, Interscience Publishers, Inc., N.Y., 1961, p. 237.

2. Ritchie, P. D., et al., J. Chem. Soc., 1955, 2717

3. Ritchie, P. D., et al., J. Chem. Soc., 1956, 3563

4. Ritchie, P. D., et al., J. Chem. Soc., 1957, 524, 2107, 2556.

5. Ritchie, P. D., et al., J. Chem. Soc., 1958, 4515.

6. Wittbecker, E. L., and Morgan, P. W., J. Polymer Sci., 40, 289 (1959).

7. Morgan, P. W., and Kowolek, S. L., J. Polymer Sci., 40, 299 (1959).

8. Lyman, D. J., and Jung, S. Lup, J. Polymer Sci., 40, 407 (1959).

9. Lyman, D. J., J. Polymer Sci., 45, 49 (1960).

V MECHANICAL PROPERTIES

The objective of this phase of the program is to determine the effect of the vacuum-thermal environment on selected mechanical properties of candidate elastomers and plastics. Three means for studying mechanical properties have been selected: (1) continuous and intermittent stress relaxation, (2) creep under constant load, and (3) tensile properties at constant strain-rate. Measurements will be performed in vacuo at 125°C over a period of three months, and for comparison, the mechanical properties of the candidate elastomers and plastics will also be measured at 125°C in helium and in air.

In order to permit correlation of results obtained in a vacuum-thermal environment with results obtained in air or in an inert atmosphere, measurements of the selected mechanical properties are made with identical test apparatuses. Since the usual assemblies for measuring mechanical properties can not be inserted in the available vacuum equipment, it was necessary to construct multiple relaxometers and creep test apparatuses. The design of the test equipment and associated instrumentation permits making measurements on samples while in a vacuum-thermal environment.

Constant strain-rate measurements with an Instron have been performed on all materials received; these tests will be repeated on samples which have been stored in the various environments. Highly standardized and reliable procedures for testing with the Instron have been developed; thus, measurements obtained on samples before and after storage in each environment afford reliable indication of the nature of the changes which the elastomeric or polymeric materials have undergone.

Stress-Relaxation Apparatus

The basic stress-relaxation test apparatus is depicted in Figure V-1. As indicated in the figure, a sample of the elastomer in the form of an accurately-cut ring is mounted between two sample holders. The upper

holder is attached to a load cell and the lower sample holder is connected to a rack; the rack's pinion is driven from a gear box to position the lower sample holder with respect to the upper so as to distend the sample ring. When the sample ring is in a relaxed position, the lower sample holder is at its highest position; this position is determined by an adjustable stop and may be detected electrically by its making contact with the stop. When the sample ring is in its strained position, the lower sample holder is in contact with a lower stop; this is also detected electrically. The position of the lower stop is adjusted at the beginning of the series of tests so as to correspond to a predetermined elongation. The gear-box drive for the rack and pinion is actuated by a crank rod which is mounted in an O-ring sealed spherical bearing; this assembly permits circular and lateral motion as well as rotation about the shaft's central axis (see Figure V-2). Each relaxometer assembly is mounted inside a heater made from two semicylindrical ceramic heating elements supported on a fired lava base as indicated in Figure V-1. A cylindrical copper sleeve (not shown in Figure V-1) prevents the sample from "seeing" the heating elements and thus promotes uniform heating of specimens. A reflector is supported at the top of the furnace to prevent the sample from "seeing" the cooled aluminum top plate. A thermocouple is mounted in the upper stop close to the sample ring. The top aluminum plate is water-cooled and protects the strain gage from the furnace's heat. Eight identical relaxometer assemblies are mounted in the vacuum chamber; another set of eight is used to make comparative tests in air, and a set of two for tests in helium. The relaxometers which are mounted in the vacuum chamber have heaters which are supplied with power from separate variable autotransformers.

Each relaxometer is equipped with a load cell made by welding a Microdot 120-ohm strain gage to a thin strip of 304 stainless steel which is clamped at one end parallel to the top aluminum plate as shown in Figure V-1. The gage is centered between the free end of the stainless steel strip and the clamp. The tension of the sample ring under elongation is transferred by a piano wire from the upper sample holder to the load cell. Since high sensitivity is desired at low deflections of the

load cell beam, a sensitive 120-ohm gage and bridge combination is required. To guard against disturbances, all apparatus is grounded and electrical circuits are shielded. All electrical connections are soldered or welded; thus, the only success of electrical noise are the wiper arm on each bridge-balancing precision potentiometer and the rotary switch in the input to the single-pen 1-mv recorder which indicates the output of the strain-gage bridges.

The bridge circuits are matched to ±0.005 ohm and are composed of ±1% deposited-carbon, 120-ohm resistors matched to ±0.005 ohm. Each bridge is individually powered by a Zener diode 10-volt d.c. power supply. The resistance bridges are immersed in a shielded, agitated oil bath mounted in a constant-temperature ($35^{o}C$) oven equipped with a blower and controlled by a bi-metal thermostat ($\pm 1^{o}C$). From preliminary tests of the materials to be investigated, it was found that loads of the order of 0.5 lb must be applied to typical elastomer specimens; a load cell beam thickness of 0.037-inch was necessary to maintain beam deflections of less than 0.025 inch. For plastic specimens, loads of 1.3 lbs are required; a beam thickness of 0.067 inch assures beam deflections of less than 0.025 inch.

The relaxometers for use in the helium environment utilize Statham 350-ohm load cells with integral 4 active-leg bridges; these are also supplied with power from Zener-controlled sources.

Creep Apparatus

Because stress-relaxation tests are applicable only to elastomeric materials, the mechanical behavior of the plastic materials in this program (Teflons, Mylar, Nylon) will be evaluated by means of constant-load tests.

The creep apparatus constructed for this program subjects dumbbell-shaped specimens of selected materials to a constant load. Elongations of specimens are determined by visual observation with a cathetometer and by photography. The creep apparatus for studies in air at atmospheric

pressure is mounted in an oven which is equipped with an observation window. The creep apparatus mounted within the vacuum chamber is equipped with heating elements, copper-Constantan thermocouples, and stainless steel shields to prevent straight-line migration of vaporized products from specimen to specimen. Provision is made for the application of loads at any time after the desired environmental vacuum-thermal conditions have been achieved. The vacuum system is equipped with observation ports to permit measurement of elongations. Duplicate unstressed dumbbell specimens will be stored in the creep apparatus for testing in the Instron at the conclusion of a test period.

Vacuum System

The large vacuum chamber visible in Figure V-3 is 3 feet in diameter and approximately 3 feet in length. The door is mounted on a track which permits its being drawn away from the chamber to an extent of 3 or 4 feet; thus, the entire contents of the chamber are easily accessible. The stress-relaxation apparatus is mounted on the door as shown in Figure V-4. The physical arrangement of the vacuum chamber and strain-gage bridge power supplies, recorders, and control console for the vacuum environment system is shown in Figure V-3.

The evacuation system consists of a Welch Duo-Seal forepump (No. 1397B), a 6-inch oil diffusion pump (CVC Model PMC-1440) with a chevron-type baffle (CVC Model BC-41) cooled to about $-30^{\circ}C$ by fluid refrigeration, and a penumatically-operated valve (CVC Type VCS-63). Suitable by-passes and ball valves permit "roughing" the vacuum chamber and "holding" the diffusion pump during preliminary evacuation procedures. A Pirani gage and an ionization gage (VG-1A) are used for measuring the vacuum in the chamber. The vacuum chamber can be evacuated to at least 3×10^{-6} mm of Hg; the ionization gage is mounted in the door of the chamber near the stress relaxation apparatus (see Figure V-4).

Apparatus for Tests in Air

Eight relaxometers and eight creep-test apparatuses are mounted in an electric oven (Freas Model 124-13, 25 x 19 x 19-inch chamber, windowed door). The relaxometers can be manipulated by a rod through a ball joint in the door (see Figure V-2). The temperature sensor normally supplied with the oven has been replaced by a thermistor temperature-sensing device, and power to the heater elements is switched by mercury-contact relays.

Apparatus for Tests in an Inert Atmosphere

Tests in an inert atmosphere are employed to assess the effect of heat and oxygen on the mechanical properties of candidate polymeric materials. Because atmospheric oxygen must be rigorously excluded, the relaxometer units are sealed in a can and a slow, steady stream of helium, or another inert gas is maintained for the duration of a test. Absence of oxygen is assured by analysis of the effluent gas with a mass spectrometer (less than 1 ppm).

A cylindrical aluminum can 16-inches in diameter and 12-inches long was constructed. Around the outside of the can was wound a 1000-watt heater element, and the whole was placed in a cylindrical Glas-Col heating unit (two 600-watt heaters). A Microtrol temperature sensing element was coiled around the inside of the can; the sensing element controls the 1000-watt auxiliary heater through a variable transformer; the Glas-Col heater is controlled manually by a variable transformer. With appropriate settings of the temperature of the Glas-Col heater and the temperature sensing element, temperature within the can is uniform to within $\pm 0.6^{\circ}C$.

Two relaxometer units are mounted on a plate which is suspended inside the can in such a way that only the test specimens (with their holders) and the long, thin rod connecting them to the rack and pinions are within the can. As noted before, Statham 350-ohm load cells are used in this apparatus; they are inserted between the connecting rods and the racks, and are water-cooled.

Testing Program

Representative polymeric materials for possible long-term space use have been supplied by the Jet Propulsion Laboratory for evaluation in this program. Table V-1 shows the materials and programmed tests.

Table V-1

MECHANICAL PROPERTIES TESTING PROGRAM

Material	Vacuum, 3 mos.			Atmos., 3 mos.			Helium, 100 hrs.		
	R	C	S*	R	C	S	R	C	S
Teflon TFE	-	1	1**	-	1	1	-	-	8
Teflon FEP-100	-	1	1	-	1	1	-	-	9
Viton A(A4411A-776)	1	-	1	1	-	1	2	-	2
Viton AHV(A4411A-777)	2	-	2	1	-	1	6	-	6
Viton B (A4411A-778)	1	-	1	1	-	1	1	-	1
G.E. Silicon Rubber									
Red (SE-555)	1	-	1	1	-	1	3	-	3
Grey	2	-	2	2	-	2	4	-	4
White	2	-	2	2	-	2	5	-	5
Mylar A500	-	2	2	-	2	2	-	-	10
Mylar A200	-	1	1	-	1	1	-	-	13
Mylar A100	-	1	1	-	1	1	-	-	11
DuPont Nylon-6	-	2	2	-	2	2	-	-	12
Epoxy-polyamide EM-1000 (Bloomingdale)	-	2	2	-	2	2	7	-	7

*R = Stress Relaxation; C = Creep; S = Storage

**1-12 indicate Priority of testing

It is planned that tests in the vacuum-thermal environment and in the air environment will be of 3-months' duration, and will be conducted at 125°C. Tests in the inert atmosphere environment will be of about 100 hours' duration. Test temperatures of 150°, 175° and 200°C may be employed in addition to 125°C in the shorter duration tests, if appropriate, to accelerate the degradation of the elastomers.

The dimensions of the sample rings used in the stress-relaxation tests are nominally 1.39-inches O.D., 1.24-inches I.D., and 0.04-inches thick. Rings have been cut from all available elastomer samples, and the dimension of each ring has been accurately determined to within 0.1 mil.

The nominal dimensions of the dumbbell-shaped specimens used in the creep tests are: 0.75-inch gage-length, 0.10-inch width gage section, and 0.010 to 0.050-inch in thickness, according to available material samples. Due to space limitations in the vacuum chamber, the dumbbell-shaped specimens and holders used in this program are smaller than those ordinarily used. Consequently, preliminary creep and tensile tests have been performed on multiple dumbbell samples to establish load ranges, effective gage-lengths, and reproducibility of test data.

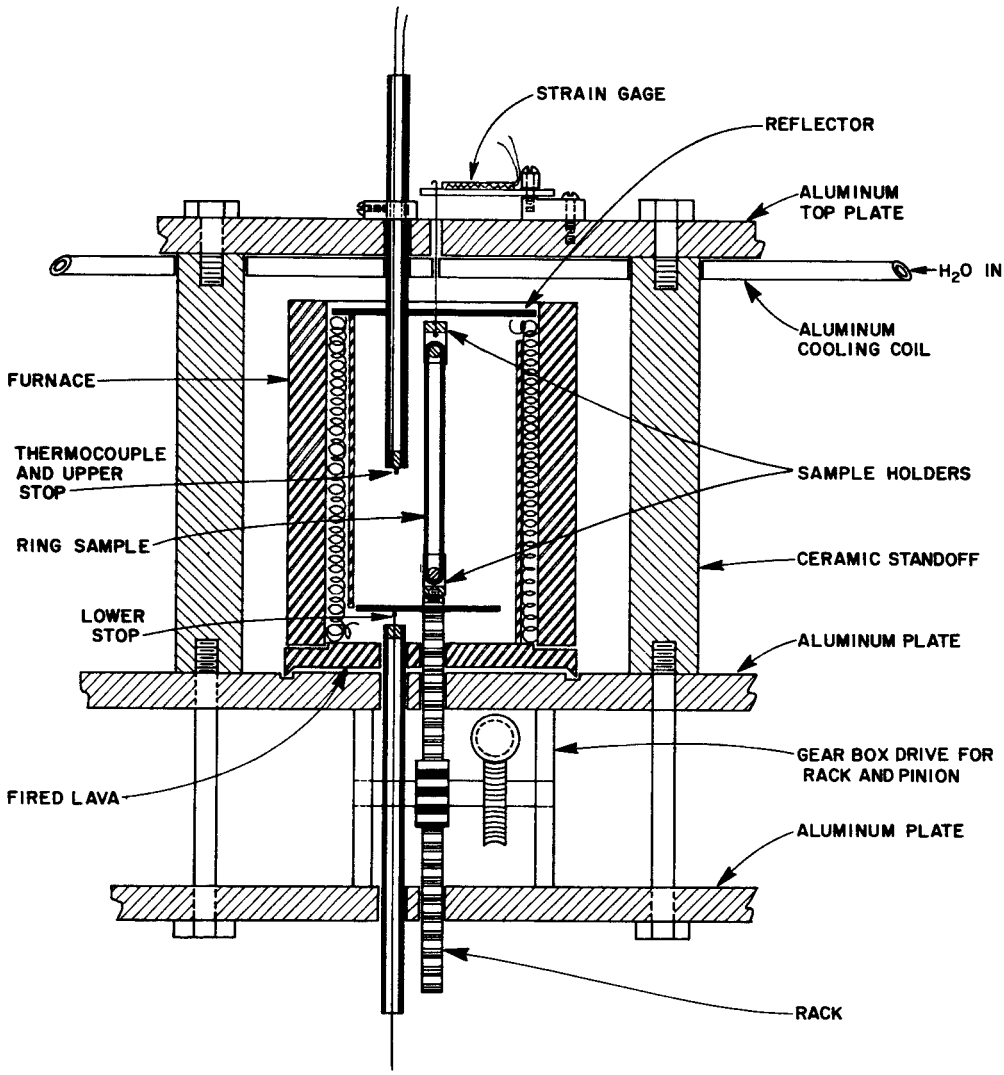
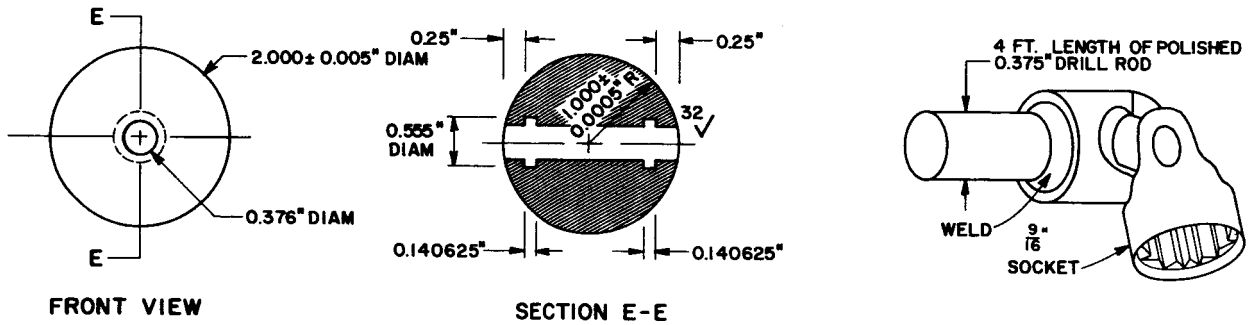


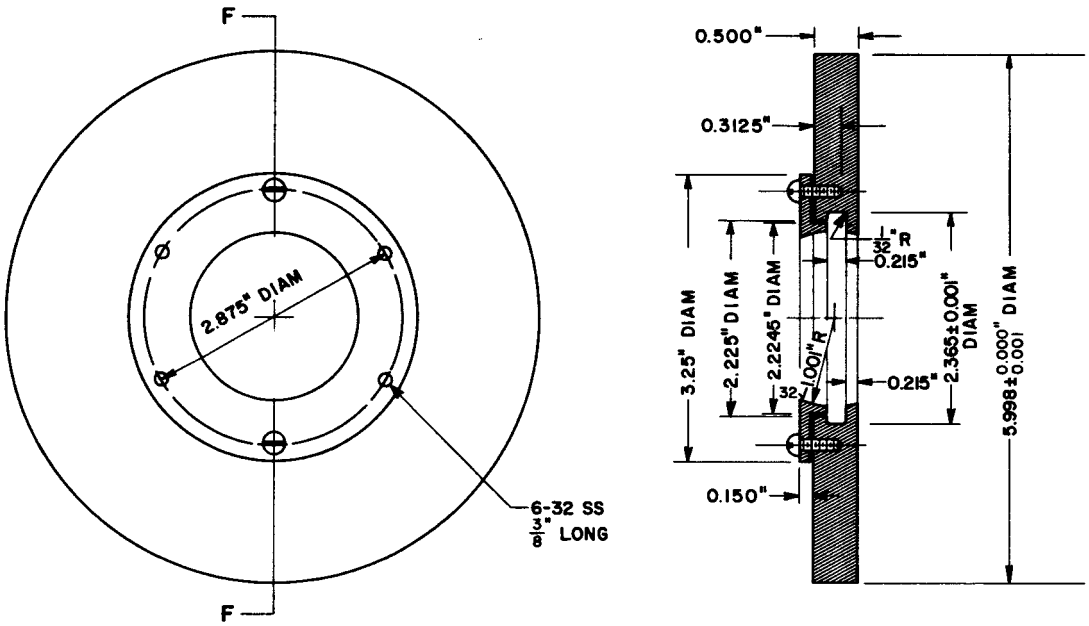
FIG. V-1 SCHEMATIC ASSEMBLY DRAWING OF RELAXOMETER



FRONT VIEW

SECTION E-E

BRASS BALL, PRECISION GROUND



FRONT VIEW

SECTION F-F

UNIVERSAL PORT

FIG. V-2 SPHERICAL BEARING AND SLIDE ROD

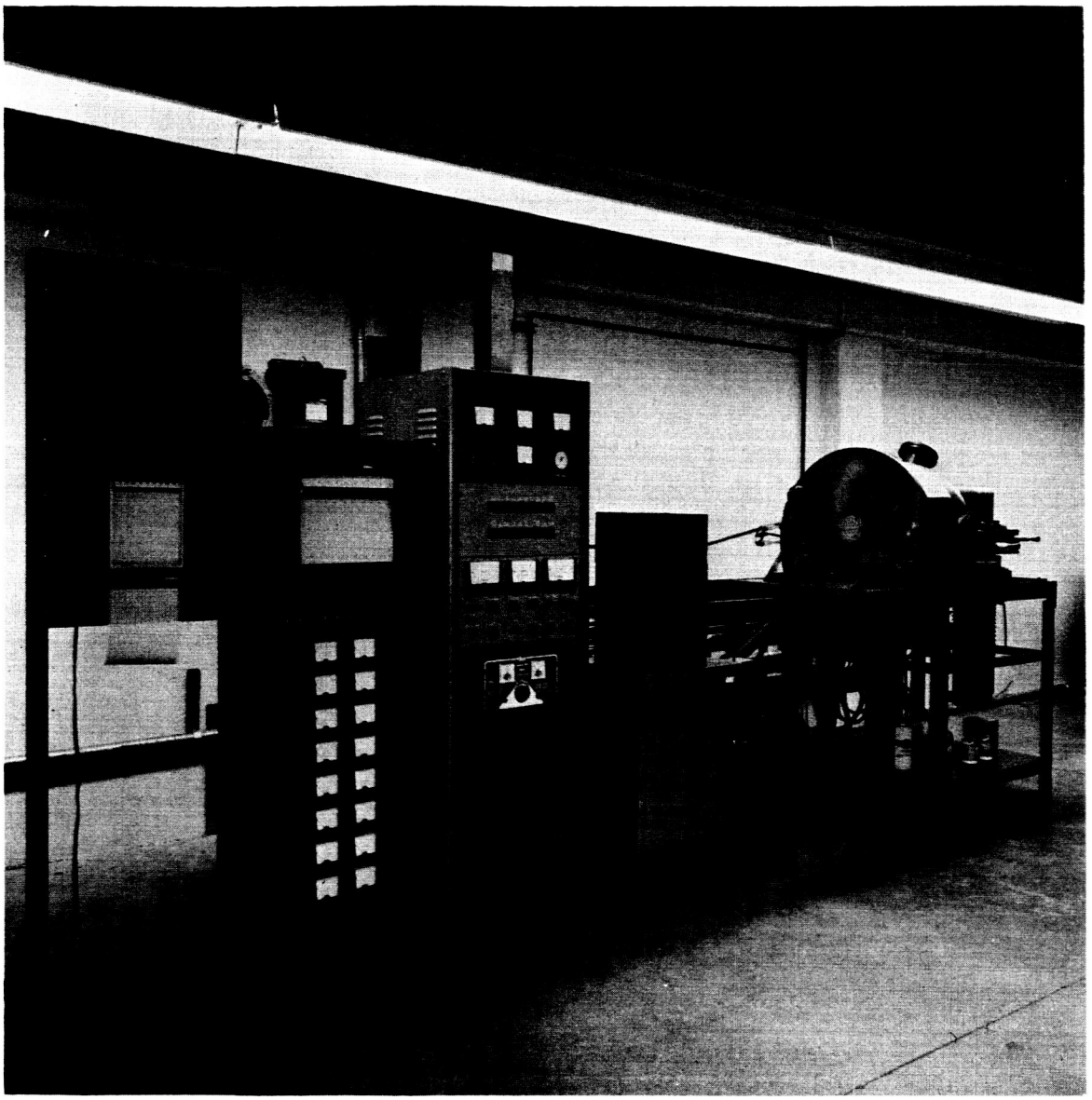


FIG. V-3 VACUUM CHAMBER WITH ASSOCIATED INSTRUMENTATION

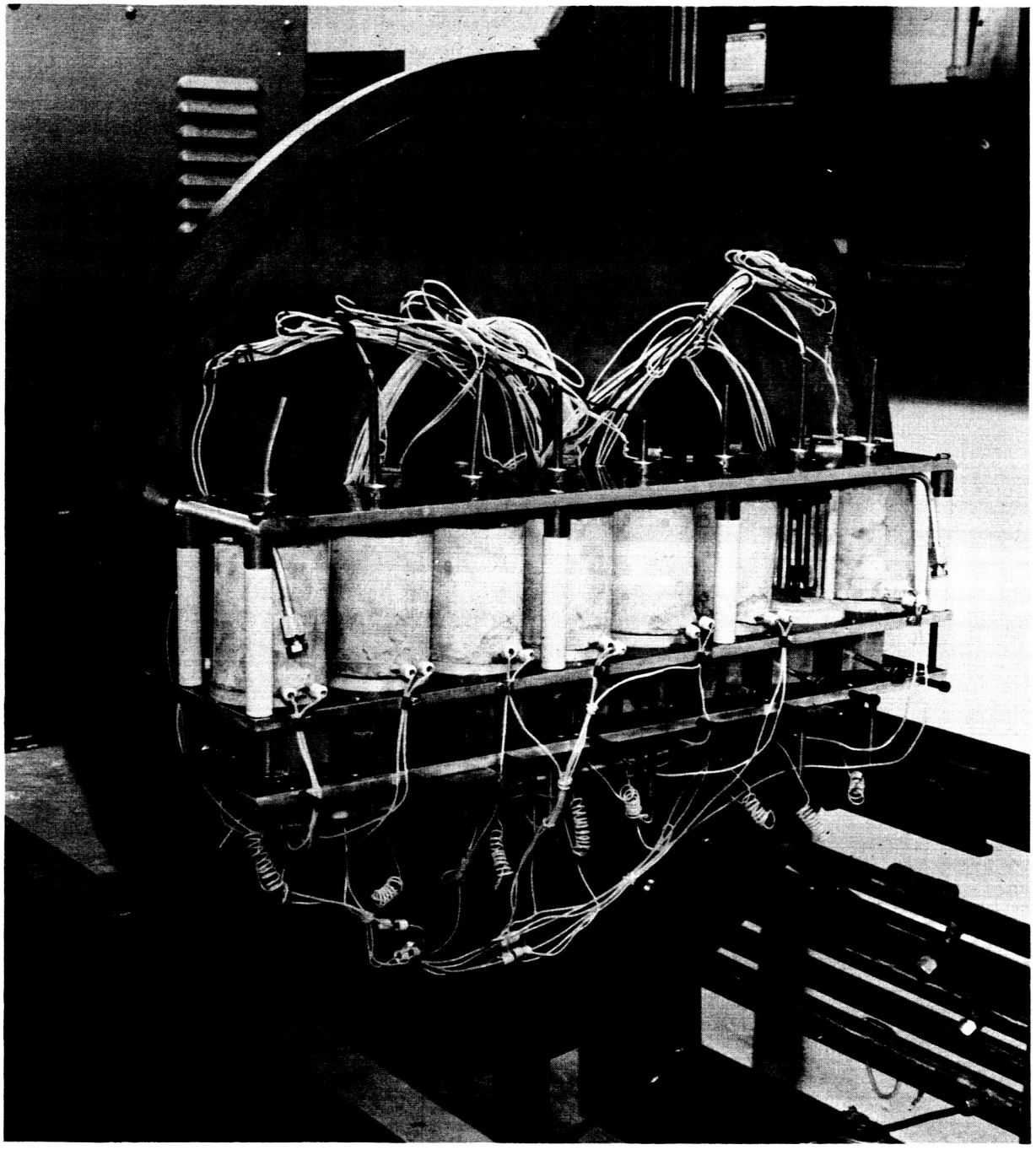


FIG. V-4 STRESS RELAXATION ASSEMBLY MOUNTED ON VACUUM CHAMBER DOOR